Combustion Chemistry for Alkenes: what have we learned from butene isomers?

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Alkenes are important intermediates formed in the combustion of larger hydrocarbons and alcohols. Moreover, liquefied petroleum gas (LPG) produced during oil refining contains a significant quantity of alkenes, particularly propene and butenes, with gasoline fuel containing butenes, pentenes, and hexenes in various amounts. Butene is the shortest alkene with structural isomers, isobutene, 1-butene, cis-2-butene, and trans-2-butene. 1-butene is the smallest unsaturated hydrocarbon having a secondary allylic carbon group and a primary carbon group which exhibit both alkane- and alkene-type chemistry. Moreover, understanding the combustion chemistry of the butene isomers is a prerequisite for a comprehensive description of the chemistry of C1–C4 hydrocarbon and oxygenated fuels. For the development and validation of combustion models, it is thus crucial to improve our knowledge of detailed C4 combustion chemistry. Building comprehensive kinetic model for butene isomers are also an extension of the work on propene.

Comprehensive chemical kinetic mechanisms have been developed to describe the combustion of butene isomers and are validated by comparison to the presently considered experimental measurements. Important reactions, highlighted via flux and sensitivity analyses, include: (a) hydrogen atom abstraction from butene isomers by hydroxyl and hydroperoxyl radicals, and molecular oxygen; (b) radical–radical recombination reactions, including 1- and 2-methylallyl radical self-recombination, the recombination of 1- and 2-methylallyl radicals with hydroperoxyl radicals; and the recombination of 1- and 2-methylallyl radicals with methyl radicals; (c) addition reactions, including hydrogen atom and hydroxyl radical addition to butene isomers ; and (d) 1- and 2-methylallyl radical decomposition reactions. The current mechanism accurately predicts the IDT and LFS measurements presented in this study, as well as the JSR and flow reactor speciation data already available in the literature.

The differences in low-temperature chemistry between alkanes and alkenes are also highlighted in this work. In normal alkanes, the fuel radical $\dot{R}$ adds to molecular oxygen forming alkylperoxyl ($R\dot{O}2$) radicals followed by isomerization and chain branching reactions which promote low-temperature fuel reactivity. However, in alkenes, because of the relatively shallow well (~20 kcal mol–1) for $R\dot{O}2$ formation compared to ~35 kcal mol–1 in alkanes, the $\dot{R} + O2 \rightleftharpoons R\dot{O}2$ equilibrium lies more to the left favoring $\dot{R} + O2$ rather than $R\dot{O}2$ radical stabilization. Based on this work, and related studies of allylic systems, it is apparent that reactivity for alkene components at very low temperatures (< 800 K) emanates from hydroxyl radical addition followed by addition of molecular oxygen to radical. At intermediate temperatures (800–1300 K), alkene reactivity is controlled by hydrogen abstraction by molecular oxygen and the reactions between resonantly stabilized radicals and hydroperoxyl radicals which results in chain branching. At higher temperatures (> 1300 K), the reactivity is mainly governed by the competition between hydrogen abstractions by molecular oxygen and $\dot{O}H$ radicals.